

SHELL PELLET HEAT EXCHANGE RETORTING - SPHER - AN ENERGY INTENSIVE, ENERGY EFFICIENT
PROCESS FOR RETORTING OIL SHALE

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INTRODUCTION

Oil shales of primary interest for surface processing occur mainly in the Piceance Basin of western Colorado. These shales contain, typically, ten to 20 percent weight of hydrocarbons recoverable by simple pyrolysis.

Process research and development in shale oil production has gone on for decades, but the once plentiful supply of low cost petroleum crudes made the economics of such processes very unfavorable. The recent shortages and cost escalation of petroleum crudes have renewed interests in "unconventional" raw material sources such as coal and oil shale.

Several processes for above ground retorting of oil shale, which have been under development for some time, include the TOSCO-II, PARAHO, and Union technologies.¹⁾ Shell had particular interests in the first two. The TOSCO (The Oil Shale Company) process uses hot balls to heat preheated shale in a rotary kiln to retorting temperatures. The shale is preheated during staged, pneumatic transport using flue gas from the retort ball heater. The PARAHO retort is a vertical kiln employing a downward moving rock bed with upflowing recycle gas and combustion products which sweep retorted hydrocarbons from the vessel. The Union process is similar but utilizes an upward flow of crushed shale. Shale is introduced at the bottom of the kiln and pushed upward by an air lock, mechanical "rock pump". Fluidized bed retorting of oil shale was proposed in the early fifties but was never developed to a commercial state.

The TOSCO-II process is capital intensive because it requires a large volume of heating gases and mechanically complex equipment; the PARAHO and Union processes are also capital intensive because they have long residence time requirements that entail massive hardware. The PARAHO process is, however, heat efficient as a result of countercurrent shale and gas flows. But the TOSCO process, although having some degree of heat recovery, uses heat relatively inefficiently.

The purpose of this work was to develop a new retorting process of relatively low capital cost that is mechanically simple, highly reliable, and uses heat efficiently. The process, ⁽²⁾ termed SPHER for Shell Pellet Heat Exchange Retorting, is a fluidization bed process conceived for the retorting of oil shale. The fluidization mode referred to in this discussion applies to a range of superficial gas velocities between those used for riser transport and dense bed operation in processes such as catalytic cracking. By this mode, shale can be made to flow upward, countercurrently to larger heat-carrier pellets that fall through the fluidized mixture. This counterflow of heat-carrier pellets and relatively coarse shale particles is the basic idea around which novel, small sized, thermally efficient and economically viable processes have been conceived. Other feedstocks to which SPHER may have potential applicability include numerous coals, lignite, wood and bark waste, agricultural residues, biotreater sludges, and industrial and municipal solid

wastes. Some specific process descriptions, with some variations, are discussed below.

Brief Description of Process Applied to Oil Shale

The SPHER process as originally conceived is shown schematically in Figure 1. This conceptual design produces 55,000 bbl/day (7575 t/d)* of raw shale oil from 66,000 ton/day (60,000 t/d) of 35 gal/ton (13.6%) oil shale. It can be seen that there are two loops for circulation of heat carrying balls. The cool ball loop carries heat from the heat recovery column to the preheater. The hot ball loop carries heat from the ball heater to the retort.

Shale is crushed or ground to a fluidizable size; preferably as large as is compatible with heat transfer requirements and ready separation from heat-carrying balls. Initial work indicates that 1/16-inch (1.6 mm) minus shale and 1/4 (6 mm) or 5/16 (8 mm) inch balls are desirable.

The shale is preheated in a fast-fluidized (entraining) bed by outer loop, heat-carrying balls that rain through the bed in countercurrent fashion (Figure 2). With air as the fluidizing medium, preheating is limited to about 600°F (315°C) because there is danger from auto-ignition, which is time, temperature, and oxygen dependent.³⁾ With other nonoxidizing gases, preheating is limited to about 650°F (343°C) by the onset of kerogen pyrolysis.

In a dense-phase fluidized bed the preheated shale is further heated to and held at the retorting temperature for sufficient time to complete the pyrolysis reactions (Figure 3). The total inventory of shale in the retorting vessel is determined by the required residence time for complete kerogen conversion and the shale throughput. The retort heat requirements are supplied by ceramic balls which circulate in the inner loop. They are reheated in a separate vessel which may operate as a moving bed, raining pellet bed, or entrained flow heater.

The spent shale is cooled in a fast-fluidized bed by the recirculated cool pellets from the preheater. In this manner, countercurrent flow of heat carriers and the shale assures efficient energy utilization. This characteristic is a prime advantage of the process.

Most conditions and features of the conceptual process are chosen to assure high throughputs (small equipment) and hence relatively low capital and fixed costs. These include the choice of flow regimes, heat carriers (density and heat capacity) and the solids-to-gas weight ratios. Attendant features of the process, such as baffle design and gas routing, are chosen to achieve operability and optimum operation.

Segregation of the two ball loops permits the tailoring of the ball material, shape and size to each specific task. Circulation of balls in the outer loop is a relatively low temperature operation and is dedicated to heat transfer. Therefore, desired ball properties include high heat capacity, small size or large heat transfer surface, erosion resistance, and low cost. Hence, a pea gravel may be suitable. Corrosion resistance may not be needed unless condensation occurs in the heat recovery section. The use of the smallest balls separable from the shale increases heat transfer and reduces the size of the exchange vessel required.

In contrast, circulation of balls in the inner loop involves the ball heater and retort where high temperatures and longer residence times are required. Reaction rate rather than heat transfer is expected to be the controlling factor in the retort design. In order to achieve the residence time needed for high conversion

*ton=2000 pounds, t=metric ton= 1000kg.

a pseudo plug-flow device such as a rotary kiln or a staged, dense-phase fluidized bed may be desirable. Since heat transfer is not controlling, the balls can be larger for easier separation from shale but they must still be small enough to permit pneumatic transport. These inner loop balls must also be resistant to thermal shock, chemical attack by the hot gases and spent shale and exposure to high temperatures. Thus, the choice of the inner loop balls is limited to materials such as ceramics.

Detailed Process Description

A more process oriented schematic of the process is shown in Figure 4.

Shale Feed Preparation

Shale preparation for SPHER requires more energy than it does for processes such as TOSCO-II in that the larger crushed shale used in TOSCO-II, e.g., 1/2-inch (13mm) minus, must be reduced to a readily fluidizable size, e.g. 1/16-inch (1.6mm) minus, for use in SPHER. Grinding by separating and recycling coarse shale is expected to produce a better size range with less fines than once-through grinding is for the same maximum particle size. Separation of shale with the desired size from oversized material may be accomplished by elutriation with gas or by screening. The recovered coarse shale is conveyed back to the grinder. Shale with the desired top size may then be pneumatically transported to a feed hopper or standpipe.

Preheater

Figure 2 is a schematic of the preheat section.

Ground raw shale is allowed to slide into or is pneumatically transported (a minimal volume flow) into the lower part of the preheater. A standpipe of shale serves as a resistance seal to purging gas and allows the preheater to be pressurized by transporting gas. Although a slide valve near the bottom of the standpipe should provide adequate flow control for the shale, a flapper valve, screw feeder, or rotary lock may be considered as options.

The shale is carried up, countercurrent to the raining pellets, as a fast-fluidized bed by compressed gas (air or mixtures of air and flue gas or recycle process gas). The preheated shale is then recovered at the top of the preheater in high-efficiency, high-load cyclones. Extremely fine dust may be carried by elutriation to the ball heater when air or air containing mixtures are used for conveying. Thus, the energy content of even the finest shale dust can be recovered without requiring expensive dust-control equipment during the preparation of shale for retorting. As conceived, the use of standpipes and proper routing gas streams reduces the necessary number of air and gas compressors and also aids in heat recovery. In this fashion, pressure balance across the whole system is achieved with sufficient extra pressure differential available for process control.

Warm ($\sim 625^{\circ}\text{F}$, $\sim 330^{\circ}\text{C}$) balls, pneumatically transported from the heat recovery section, are recovered at the top of the preheater by a cyclonic separator into a surge hopper. From the hopper they are admitted in controlled flow to the upper part of the preheater through an appropriate control valve and steam purge system. A conical (or other shaped) deflector is desirable to disperse the ball stream uniformly. Balls fall under the influence of gravity against the rising stream of fast-fluidized shale. The range of conditions under which countercurrent flow will exist is being studied. The smallest balls, i.e., those with the highest surface-to-volume ratio, that will fall sufficiently fast through the preheater at an economical shale mass flux are desirable for effective heat exchange.

Balls collecting at the bottom of the preheater in an appropriately dimensioned boot are stripped of shale particles by elutriating gas. Under ideal

conditions, the largest shale particles that can be readily elutriated from between the pellets are about half the size of the pellets. In practice the separation is more efficient when the ball/shale size ratio is 4-5. Balls drop by controlled flow into a transport line where they are pneumatically conveyed to the shale heat recovery section.

The countercurrent raining-ball/fast-fluidized flow regime must be operated so that staging is effected, i.e., backmixing must be effectively retarded. Temperature approaches were initially assumed to be 75°F (42°C) at the top and 50°F (28°C) at the bottom of the preheat vessel. Any increase in holdup of the balls in contact with shale will reduce the height of vessel required. Increased staging and holdup of balls are both accomplished by a system of baffles and/or grid plates. With such designs it is important to avoid dead hot spots where shale might accumulate because spontaneous ignition of shale might occur if air is used as the transporting gas.

Due to vaporization of water in the preheater it may be desirable to increase the diameter of the preheater with increasing height to maintain relatively constant flow conditions. At proposed preheater temperatures, the short residence time in the preheater should allow air to be used as a transporting gas without spontaneous ignition and with little shale degradation and yield loss. Dilution of transport air with flue gas may be used to permit a higher preheating temperature without ignition. The use of air as the entraining gas in the preheater permits the finest oil shale dust and any prematurely evolved hydrocarbons to be economically burned in the ball heater. Thus, combustion air is also preheated in the shale preheater. By operating the preheater in counterflow with a temperature approach of <100°F (55°C), overheating of small particles is avoided.

Retort

Figure 3 depicts the retort section of the raining pellet process.

Shale entrained from the preheater is fed to the lower portion of the retort through a high-load, high-efficiency separator and surge hopper (with aeration). The shale feed rate to the retort is controlled in the same way as it is to the preheater.

Steam or gas injection is required at the bottom of the retort to start the fluidization. However, some or all of this gas may be first used in the ball stripping section. Vapor emitted by retorting adds greatly to the volumetric flow of fluidizing gas as it rises up through the retort. The vessel cross-section is increased accordingly to maintain constant conditions for the dense fluidized bed.

Hot heat carrying balls (at about 1400°F, 760°C) are added to the top of the retort in the same manner as they are to the preheater, but in separate streams to different levels in the retort. This avoids overheating (and cracking) at the top of the retort. The ball diameters should be about 1/4-inch (6mm) to assure a reasonable fall velocity (0.25 fps, 0.08m/s) through the dense-phase fluidized bed of shale.

The balls collect in a boot at the bottom of the retort and are stripped of shale fines in an elutriating section. Superheated steam (1200°F, 650°C) provides both the stripping action and the feed shale fluidizing action. The cooled balls (900°F, 480°C) are then recirculated pneumatically to the ball heater for reheating. Air for the ball lift is combined with air from the preheater cyclones and with a third air/fuel-gas stream to provide the desired fuel mixture for the ball heater.

Processed shale is removed at the top of the retort. A circumferential weir is provided to maintain a constant bed height in the upper stage. Entrained shale particles are removed from the product vapor by high-efficiency cyclones

located in the vapor disengagement section. The dimensions of this top section are, in fact, determined by the cyclone configuration. Superheated steam (1200°F, 650°C) is injected in an effort to eliminate condensation coking in the vapor section.

Adsorbed and entrained vapors are removed from the retorted shale by steam in the spent shale stripper. Stripped shale is sent to the heat recovery section. The overhead products from the spent shale stripper are combined with the retort vapors and are further superheated with steam to reduce condensation coking and quenched with fractionator bottoms in a quench tower.

Staging of the retort can reduce the average residence time required for a given hydrocarbon yield. This staging could be achieved by adding restrictive horizontal grids spaced, for example, at ten-foot intervals of height. However, since staging may also introduce an unwanted temperature gradient across the retort, a single-stage design may be favored.

Pyrolysis data indicate that a relatively long (several minutes) residence time is required for the retorting reaction⁴). Hence, heat transfer is not limiting in the retort and larger balls with a lower surface-to-volume ratio may be used. Larger balls are desirable because, *inter alia*, their manufacturing cost is less. The maximum ball diameter is limited by the ability to transport them pneumatically and by their settling velocity through the fluidized bed of shale. Thermal shock could also be a factor that limits ball size. About 1/4-inch (6mm) diameter balls may be a good compromise on size, as mentioned above.

Ball Heater

The ball heater can be a moving bed, a raining pellet or an entrained flow design. Preheated air from the ball lift pipe plus air from the preheater and supplemental air and fuel form the combustion mixture used to heat the balls. Ball heater flue gas is routed partly to a waste heat boiler to recover energy in the form of high-pressure steam and partly to other vessels in the process to serve as a transport gas. Cooled gases are then scrubbed to remove both particulates and any sulfur oxides. The particulate shale dust naturally absorbs sulfur oxides in the wet scrubber. Exiting hot balls return to the retort through several feed standpipes.

Heat Recovery

The heat recovery section is similar to the preheat sections.

Fast-fluidized retorted shale is cooled from 990°F (482°C) to about 175°F (79°C) by contacting it countercurrently with balls from the preheat section. Since the conveying (flue) gas is cooled and contracts as it rises, it may be desirable to reduce the vessel size accordingly in the upper portion to maintain the desired flow rate of gas.

Elutriated cooled shale is separated in a high-efficiency separator and routed to a moisturizer in preparation for disposal. Gas from the heat recovery unit is water washed in a venturi scrubber and excess water from the scrubber is used in the moisturizer. Little water vapor is generated in scrubbing the gas and wetting the spent shale because the outlet temperature of the heat recovery unit is low (175°F, 79°C). Water usage in the SPHER process is, therefore, desirably low.

Problem Areas

Since SPHER represents the application of new regimes of fluidization to shale retorting, there are a number of questions that must be answered and factors that must be quantified. Some have been answered by simple experiments, the results of which would indicate either a "go" or a "no go" on future work, and some factors

will eventually require demonstration plant operation under design conditions to prove the process. Factors of primary concern are discussed below.

Heat Transfer Rates

Process evaluations have used a rate coefficient of 90 Btu/sq ft/hr °F ($0.51 \text{ kw/m}^2/\text{°C}$), based upon the surface area of the balls. Literature data on transfer from fluidized beds to submerged objects indicate that even higher rates have been achieved, but these high rates are functions of bed density and the size of the fluidized particles. Data directly applicable to the SPHER system are required for final evaluations and designs.

Flow Regimes

The countercurrent flow of pellets relative to the fast-fluidized shale and its fluidizing gas suggests the existence of limiting or flooding velocities. The impingement of shale particles upon pellets (knockback effect) retards the upward flow of shale as well as the fall of the pellets. The size of the effect is different in dense-bed and fast-fluidized regimes. In dense beds, the falling velocity of pellets will be about 1/4 fps (0.08 m/s) while in the fast-fluidized bed the falling velocity is expected to be larger. Operational windows and pressure drop/holdup equations must be defined. These phenomena have been investigated on the 7-1/2-inch (19 cm) diameter cold-flow unit. Shale flux rates of 10 lb/sec/ft^2 (49 kg/sec/m^2) and ball flux rate of 15 lb/sec/ft^2 (73 kg/sec/m^2) were achieved at superficial gas velocities of 15 to 20 ft/sec (4.6 to 6.1 m/s).

Staging

Efficient use of heat and, to a lesser extent retorting yield, require some countercurrent staging to achieve the economic advantages expected for the SPHER process. About six stages are desired for the preheater, four in the heat recovery section and two or three stages may be desired in the retort.

Gas-fluidized beds are basically unstable and they tend to have a high degree of backmixing due to circulation patterns caused by rising gas bubbles. Beds with a large height-to-diameter ratio (L/D) tend to restrict this circulation and increase the staging of fluidized solids. For example, the Shell's Anacortes CCU regenerator ($L/D \approx 2.5$) performs with about four solids mixing stages.

Pneumatic lift pipes (risers) for solids do not exhibit large eddy mixing currents but they do have radial velocity profiles that peak toward the center of the pipe. It is even possible (at lower velocities) for solids in risers to flow down along the wall. Catalytic cracking feed risers ($L/D \approx 20$) exhibit 4 to 6 solids mixing stages. The velocity profile flattens (approaches plug flow) with increasing pipe diameter but becomes more peaked with increased solids loading and decreased velocity.

Determination of staging and mixing of solids in the raining pellet system may require large test facilities.

Agglomeration and Defluidization

Two possible problems arise: (1) ground shale containing a sizeable fraction of 1/16-inch-or-less (1.6mm) particles will segregate into coarse and fine layers, even under moderate fluidization conditions, and (2) the ground shale might become tacky, due to the presence of liquids on the shale surface under retort conditions, and defluidize by agglomeration.

The question of agglomeration needs further resolution. Small scale experiments indicated direct vaporization of shale oil occurred during retorting and no

agglomeration tendencies were noted. However, agglomeration could take place in cold spots where hydrocarbon condensation might occur. Two requirements of retort design are to avoid cold spots and to provide sufficient mixing of fresh shale with inerts (i.e., with spent shale) to prevent agglomeration.

Overheating and Ignition

Air was originally conceived as the preheater gas for transporting shale but use of an inert gas may be preferred. If shale is heated in air to a temperature where retorting proceeds, then a combustible mixture is formed and ignition can occur. At atmospheric pressure this occurs at about 630°F, 332°C. Local stagnation zones of shale near the ball inlet should be avoided because they might lead to such a condition. Dilution with an inert gas or use of another gas as a carrier may be preferred because both will permit a broader range of operation without the possibility of shale ignition.

Pressure Balance - Operability

Overall operation, as in catalytic cracking, depends on use of standpipes to generate the pressure differentials necessary to cause shale and balls to flow into the process vessels. Excess pressures are taken out by slide valve control which also dampens the transfer of pressure surges between vessels.

The high permeability of the standpipe material, especially of the spheres or pellets, will allow appreciable gas leakage. Adequate purge gases in the standpipe will, therefore, be required.

Ball Separation and Recovery

The raining balls must be stripped free of shale before being removed from a vessel. This can be most readily done by use of a stripping gas at relatively high velocity (≥ 10 fps, 3 m/s) in a ball-collection boot. This might be a large fraction of the fluidizing gas in a vessel and reduces the quantity of gas available for transferring shale into the vessel above the boot.

Generation of Fines and Entrainment of Shale

Although retorting of shale does not, in itself, generate fines it does weaken the particles so that they are more readily attritable. Particle size distribution reported for a fluidized bed process is listed in Table 1. This potential generation of fines may not be serious for SPHER since operation will be once through for the shale and residence time in vessels with fluidized beds is only a few minutes.

Entrainment of shale in gas in the preheat and heat recovery sections is the basic mode of transport for shale. In the retort, excessive entrainment reduce the residence time below that needed for retorting and extra steps may be required for returning shale fines to the retort.

In all cases, high-load and high-efficiency (cyclone) separators will be required to prevent excessive carryover of shale in gas streams to other portions of the process. These recovered fines may need to be recycled to the appropriate vessels in order to insure the proper concentration of fines for smooth fluidization.

Choice of Ball Material

The purpose of the balls is to provide a means of conveying and exchanging highly concentrated heat energy. Thus, they should have a high external surface area (i.e., a small diameter) and a high heat capacity. However, they must be large enough to be readily separable from the shale. For ease of separation they should have a high density. Table 2 lists some properties of candidate materials. Other factors

to consider include cost and resistance to corrosion, abrasion and thermal shock. The quality of a material such as alumina is highly dependent upon its method of manufacture and the suitability of specific aluminas must be defined.

Erosion/Attrition/Thermal Shock

The high velocities of balls in lift pipes and the turbulent nature of the fluidized beds lead to the possibility of erosion of the equipment and attrition or fracturing of the balls. Erosion can be reduced by using abrasion resistant refractory linings in pipes. Attrition and fracturing of balls can be reduced by proper design to reduce the effect of impaction at elbows and on deflection plates.

Breakage by thermal shock is reduced by countercurrent operation, which allows reduced temperature gradients, and by a small ball size, which reduces thermal stresses.

Conclusions

As with most newly conceived processes there is considerable development work to be done before SPHER is a mature process. This report serves to present the basic features of SPHER and to point up some areas requiring development work.

References

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2. U. S. Patent No. 4,110,193, dated August 29, 1978.
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5. U. S. Patent No. 2,717,869, dated September 13, 1955.

TABLE 1. PARTICLE SIZE DISTRIBUTIONS OF SHALE RETORTED BY TOSCO
AND FLUIDIZED BED TECHNIQUES

<u>Fluidized Spent Shale^{a)}</u>	
<u>Size Range, μ</u>	<u>Percent</u>
0-20	<25
20-60	5-15
60-200	20-50
200-400	20-30
<400	<5

a) See Reference No. 5

TABLE 2. PROPERTIES AND CIRCULATION RATES OF
CANDIDATE MATERIALS FOR OUTER BALL LOOP

<u>Material</u>	<u>Density</u>		<u>Heat Capacity</u>		
	<u>lb/ft³</u>	<u>t/m³</u>	<u>Btu/Lb°F</u>	<u>Btu/Ft³°F</u>	<u>Kcal/m³°C</u>
High Density Alumina (ceramic balls used by Tosco)	231	3.70	0.22	50.8	814
Aluminum	168	2.69	0.23	38.8	622
Steel	487	7.80	0.12	58.4	935
Lead	686	10.99	0.03	20.6	330
Gravel	156	2.50	0.2	31.2	500

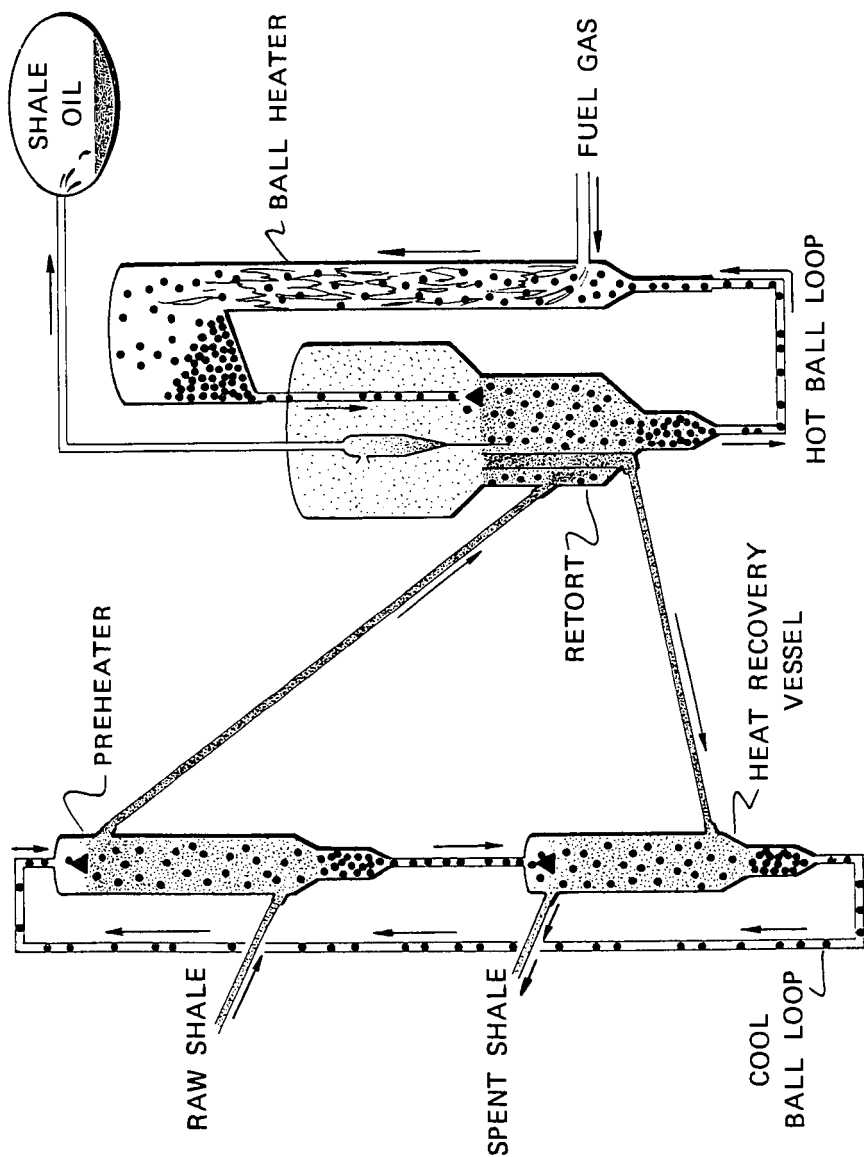


Figure 1. Spher Oil Shale Process

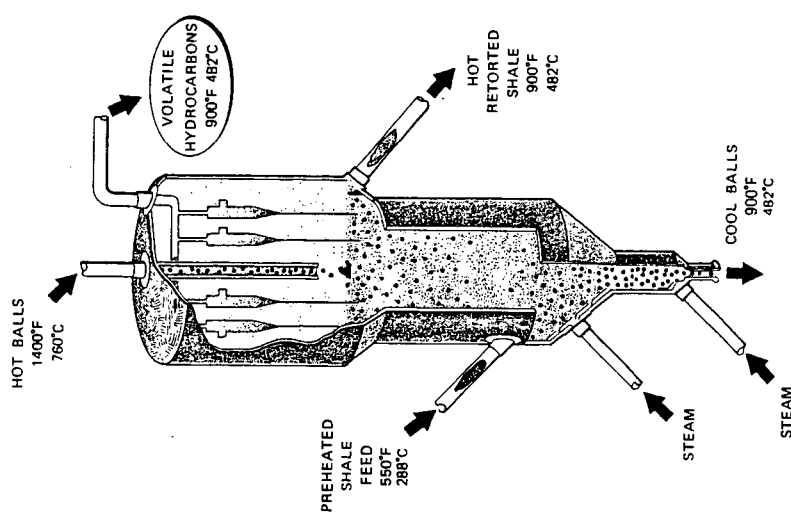


Figure 3. Spher Retort

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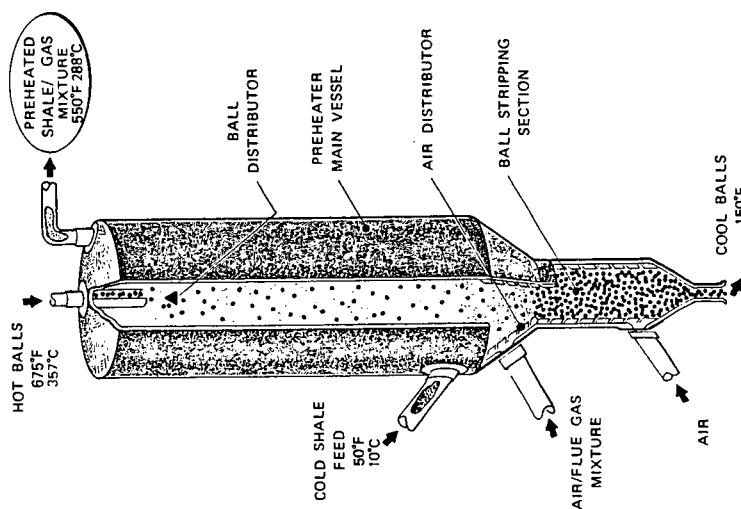


Figure 2. Spher Preheater

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